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Effect of Charged Conditions of Stabilizers for Cadmium Sulfide Microcrystalline Photocatalysts on Photoreduction of Carbon Dioxide

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The use of stabilizers having negative charges such as polyacrylic acid for CdS microcrystals in aqueous solutions yielded selectively formate as a photoreduction product of CO_2, while positively charged stabilizers such as polyethyleneimine worked well for selective production of CO. Furthermore, it was found that the rate of photo-induced reduction of carbon dioxide was influenced by the amount of charges of the stabilizers used.

ZnS1-4) and $TiO_2$5, 6) microcrystals possess higher activities than the corresponding bulk materials for photo-induced reduction of CO_2. In cases of using such small semiconductor particles as to show size quantization effects as photocatalysts, the use of stabilizers are required to prevent agglomeration of the particles. So far, various stabilizers have been used, but only a limited number of studies have investigated the effect of the structure7) and the charges8) of the stabilizers on the activities as photocatalysts of the size quantized particles. It has already been reported9) that the stabilizers influence the rate of photo-induced reactions on the size quantized particles, but no publication is available concerning another work of the stabilizers that they can change the photo-induced reaction routes. In this letter, we would like to report that photoreduction products of CO_2 were different depending on the kind and the charged conditions of the stabilizers used.

CdS microcrystals were prepared under nitrogen atmosphere by mixing in an equal volume 4×10^{-4} M (= mol dm^{-3}) sodium sulfide with 6×10^{-4} M cadmium perchlorate containing a stabilizer with a monomeric concentration of 8×10^{-4} M. Polyacrylic acid (MW=150000), poly(sodium vinylsulfonate) (averaged molecular weight (MW)=1100), and poly(sodium 4-stylenesulfonate) (MW=70000) were used as anionic stabilizers, and poly(allylamine hydrochloride) (MW=70000), polyethyleneimine (MW=70000) and polybrene(MW=22500) were used as cationic stabilizers. The CdS microcrystals with these stabilizers were stable at least for 3 weeks. The charged conditions of the stabilizers in solution was evaluated using the well-established technique of potentiometric titration10) of 0.01 M NaOH aqueous solution containing various stabilizers whose monomer concentration was 0.01 M with 0.01 M $HClO_4$.

If acid-base equilibrium is represented by the following equation for anionic and cationic stabilizers, respectively,

$$RH = R^- + H^+ \qquad\qquad RH + H^+ = RH_2^+ \qquad\qquad (1)$$

then the fraction of the negative charges (N) and positive charges (P) of the stabilizers is given by

$$N = \frac{[R^-]}{[R^-] + [RH]} \qquad P = \frac{[RH_2^+]}{[RH] + [RH_2^+]} \qquad (2)$$

where $[R^-]$, [RH], and $[RH_2^+]$ show the concentration of the respective species on the monomer basis.

The photoreduction of CO_2 was carried out using a quartz cell (1 x 1 x 4.5 cm^3) having a side branch. 4 cm^3 of various CdS microcrystalline colloids was put in the cell, and 0.1 cm^3 of 0.16 M stabilizer on the monomer basis was added. 1 M 2-propanol was used as a holescavenger. pH of the solution was adjusted to 5.5 by addition of 1.5 mM $NaHCO_3$, followed by bubbling of CO_2 for 20 min. Illumination was carried out at 0.51 W cm^{-2} using lights of wavelengths longer than 310 nm prepared by passing lights from a 500 W Xenon lamp through a UV-33 glass filter (Toshiba). The photoreduction experiments were carried out in a water bath at 303 K under magnetically stirring the solution. Hydrogen and CO produced in the gas phase and acetone produced in the liquid phase were determined by gas chromatography. Formate produced in the liquid phase was determined by liquid chromatography.

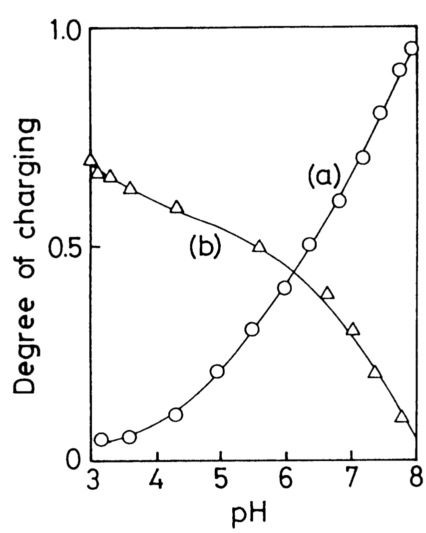

Fig. 1. Degree of charging of (a) polyacrylic acid and (b) polyethyleneimine as a function of pH.

Figure 1 shows the degree of charging for polyacrylic acid and polyethyleneimine determined from eq. (2) as a function of pH. From each curve of this figure, the degree of charging of polyacrylic acid and polyethyleneimine at pH 5.5, at which the photoreduction experiments of CO_2 were carried out, was 0.30 and 0.50, respectively. The degree of charging at pH 5.5 for the other stabilizers was evaluated in the same way. The degree of negatively charging was 0.97 and 1.0 for poly(sodium vinylsulfonate) and poly(sodium 4-stylenesulfonate), respectively, while the degree of positively charging was 0.98 and 1.0 for poly (allylamine hydrochloride) and polybrene, respectively.

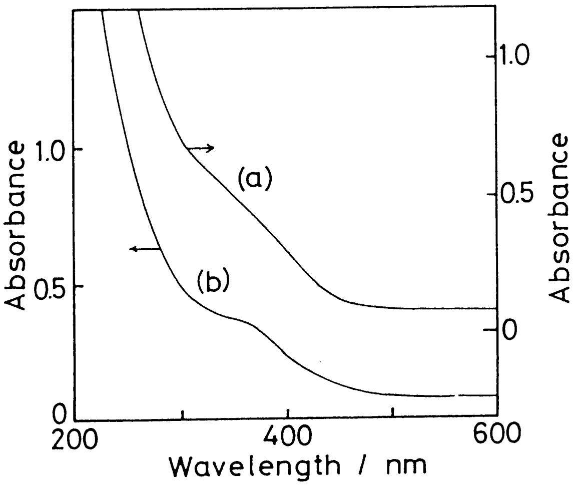

Fig. 2. Absorption spectra of CdS microcrystals stabilized by (a) polyacrylic acid and (b) polyethyleneimine. [CdS]=2 x 10^{-4} M.

Absorption spectra of CdS microcrystals in the presence of polyacrylic acid and polyethyleneimine are shown in Fig. 2. Both spectra gave the absorption onset at wavelengths much shorter than ca. 520 nm which is valid for the bulk CdS particles, suggesting that the quantized microcrystals were prepared. Judging from a theoretically derived relation between the particle diameter and the bandgap,[11] CdS microcrystals prepared in the present study were less than 5 nm in the diameter. If the bandgap (E_g) of CdS microcrystals in the prepared colloids were evaluated by applying their

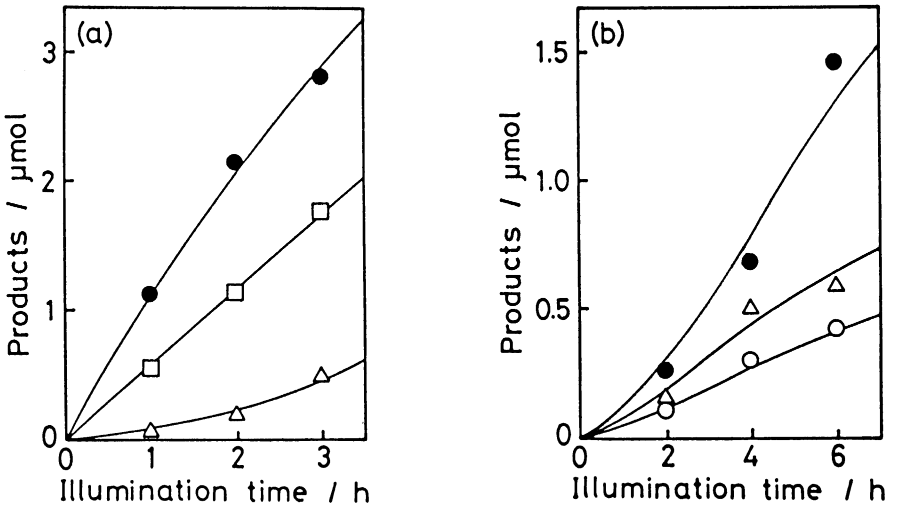

Fig. 3. Time course of the production of (□) formate, (○) CO, (△) hydrogen and (●) acetone using the 2 x 10^{-4} M CdS microcrystals containing 1 M 2-propanol in the presence of 4 x 10^{-3} M (a) polyacrylic acid and (b) polyethyleneimine on the monomer basis.

absorption spectra to $(\sigma h\nu)^2$ vs. hν relation,[12)] where σ is the molar extinction coefficient, results given in Table 1 were obtained.

Figure 3 shows the time course of the production of reduction and oxidation products for CO_2-saturated solution containing 1 M 2-propanol in the presence of polyacrylic acid and polyethyleneimine. As this figure shows, formate was obtained as a major product of the CO_2 photoreduction when polyacrylic acid was used as the stabilizer, while CO was obtained with the use of polyethyleneimine. In both cases, hydrogen was evolved as another reduction product and acetone was a sole oxidation product. Blank experiments confirmed that no reaction took place in the absence of CO_2 and 2-propanol. Absorption spectra of the CdS microcrystals were unchanged with illumination for 6h. These results suggest that the production of oxidation products and reduction products occurred with high chemical stoichiometry. Table 1 summarizes photoreduction experiments of CO_2 obtained using various stabilizers adopted in the present study. The results shown in this table suggest that the use of negatively charged stabilizers such as poly(sodium vinylsulfonate), poly(sodium 4-stylenesulfonate) favored the production of formate, while the use of positively charged stabilizers such as

Table 1. Results of the photoreduction of CO_2 using CdS microcrystals stabilized by various polymers

Stabilizer	E_g /eV	Illumination time / h	Reduction product /mmol		
			$HCOO^-$	CO	H_2
poly(sodium vinylsulfonate)	2.68	4	0.73	0	0.090
poly(sodium 4-stylenesulfonate)	2.66	4	0.88	0	0.046
polyacrylic acid	2.80	3	1.77	0	0.59
poly(allylamine hydrochloride)	2.80	16	0	0.75	0
polybrene	2.71	9	0	0.11	0
polyethyleneimine	2.85	6	0	0.40	0.72
polyethyleneimine[a)]	2.48	15	0	0.15	0.32

a) After standing for one month after preparation of CdS microcrystals.

polyallylamine and polybrene were effective in selective production of CO from CO_2. The CdS microcrystals stabilized by polyethyleneimine became large with storage at room temperature for one month, and the activities as the photocatalyst decreased, but the reduction products obtained were unchanged, as shown also in the table. The effect of charging of the stabilizers on the relative production rate of the reduction products of CO_2 to hydrogen was investigated by changing the pH of the solution for cases of using polyacrylic acid and polyethyleneimine, and the results obtained are shown in Fig. 4. Though the magnitude of the relative rates was different between the two kinds of stabilizers used, an increase in the amount of charges of the stabilizers favored the reduction of CO_2 either to formate or to CO.

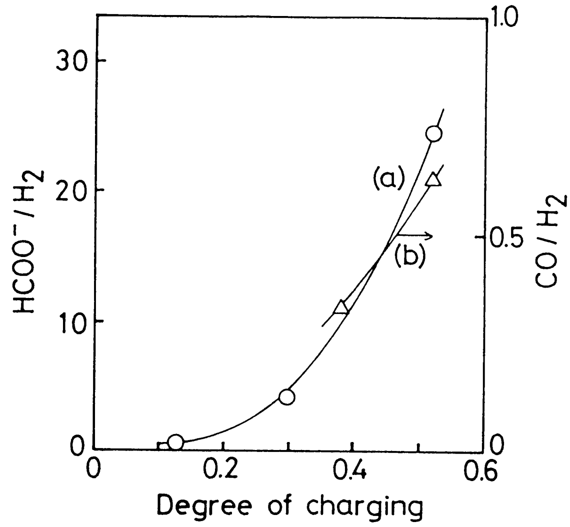

Fig. 4. Ratio of the amount of formate to hydrogen produced (a) and that of CO to hydrogen produced (b) as a function of the degree of charging of (a) polyacrylic acid and (b) polyethyleneimine.

The photoreduction of CO_2 is initiated by one-electron reduction of adsorbed CO_2 to give $CO_2^{-\cdot}$. When the photocatalyst is surrounded by negatively charged stabilizers, the resulting $CO_2^{-\cdot}$ can make adsorption onto the photocatalyst surfaces with the carbon atom of $CO_2^{-\cdot}$, resulting in the end-on type adsorption. In contrast, in cases where the photocatalyst is covered with positively charged stabilizers, the adsorption of $CO_2^{-\cdot}$ can occur with involvement of both the carbon atom and negatively charged oxygen atom of $CO_2^{-\cdot}$, resulting in the so-called side-on adsorption. The end-on type adsorption favors the formate production, while the side-on type the carbon monoxide production.$^{13)}$ The difference in the rate of production between formate and CO may result from differences in the stability of adsorbed CO_2 in these two different configurations.

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